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13. ABSTRACT (Maximum 200 Words) A number of investigations concerning the synthesis, characterization and properties of electro-optical macromolecules has been completed. A wide range of structures mostly based on a conjugated main chain and focused on providing high photo-luminescent and electroluminescent quantum yields, were produced and fabricated into opto-electronic devices. Parallel investigations have continued the long established study of polymer blends by various physical means. Amongst others, a dielectric relaxation study has compared the properties of a prototypical blend with that of a statistical copolymer of equal overall composition to probe the dimensions of micro-heterogeneity in such systems. Further studies of the below- $\Theta$ temperature collapse (coil-globule) transition in solvated polymer chains has included polyelectrolyte systems. Some 46 papers were published or were in press during the grant period.					
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**FINAL TECHNICAL REPORT**

**ELECTRO OPTICAL PROPERTIES  
OF COPOLYMER BLENDS**

**GRANT AFOSR F49620-99-1-0022**

**Period Covered: 3/15/99- 12/14/02**

**September 1, 2003**

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I. TITLE: ELECTRO OPTICAL PROPERTIES OF COPOLYMER BLENDS

II. PRINCIPAL INVESTIGATOR: Dr. Frank E. Karasz  
Polymer Science & Engineering

III. GRANT NUMBER: AFOSR F 49620-99-0022

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## VI. ASTRACT OF ACCOMPLISHMENTS

A number of investigations concerning the synthesis, characterization and properties of electro-optical macromolecules has been completed. A wide range of structures mostly based on a conjugated main chain and focused on providing high photo-luminescent and electroluminescent quantum yields, were produced and fabricated into opto-electronic devices. Parallel investigations have continued the long established study of polymer blends by various physical means. Amongst others, a dielectric relaxation study has compared the properties of a prototypical blend with that of a statistical copolymer of equal overall composition to probe the dimensions of micro-heterogeneity in such systems. Further studies of the below- $\Theta$  temperature collapse (coil-globule) transition in solvated polymer chains has included polyelectrolyte systems. Some 46 papers were published or were in press during the grant period.

## VII. DESCRIPTION OF RESEARCH UNDERTAKEN

The grant has supported several research themes in the physical chemistry of macromolecules, including some that have continued from earlier AFOSR funding. The results have in large part been published (46 papers published and in press) in the open literature, and representative highlights are discussed below.

### A. Electro-optically Active Polymers ( 1,2,3,5,7,9,13,15,16,18,21,24-26,29-34,36,38,40-46)

We have pursued an integrated research program in this area in which new polymers have been a) synthesized b) characterized, especially with respect to their photo-physical properties and c) fabricated into devices such as light emitting diodes and optically-pumped lasers. Examples are given below.<sup>1</sup>

Extensive studies have been made on organic and polymeric light emitting diodes (LEDs) because of their practical application as well as inherent scientific interest. Conjugated polymers have many advantages in terms of versatile multi-color emission controlled readily by the molecular structure and facile fabrication of small and large area active layers by spin coating or printing technology. Some problems such as polymer purity, and purification, control of polymerization and low luminance efficiency remain. To achieve an efficient polymer LED, we have also reported several types of novel electroluminescent polymers which are PPV derivatives containing bulky phenyl substituents and single hetero-atom linkages in the polymer main chain to control the effective conjugation length. Carbazole containing polymers and multi-component

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<sup>1</sup> The numbers in the section headings correspond to the publications listed in Section VIII.



systems incorporating an electron transporting polymer with an oxadiazole repeating unit to control the color tuning of the emitting polymer and are discussed below.

### Synthesis

#### a) Heteroatom-containing PPVs

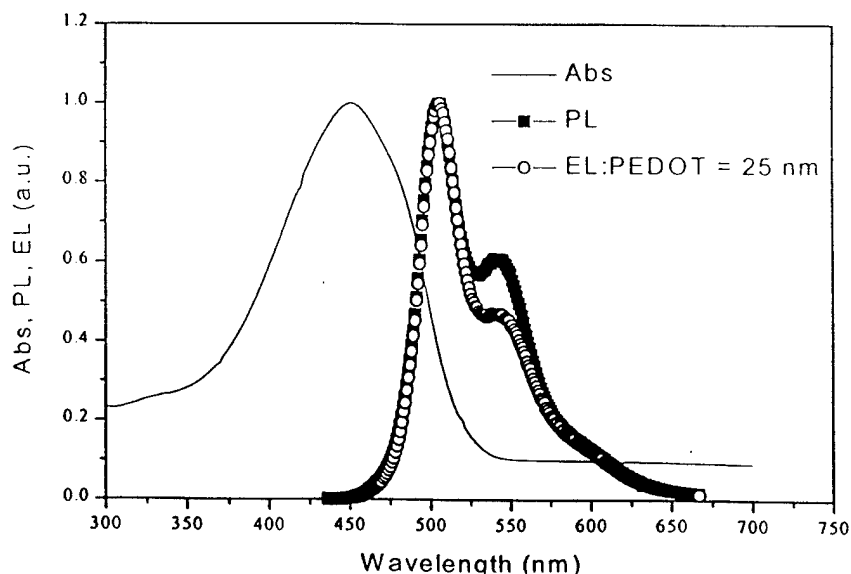
A PPV chromophore containing a long chain alkylsilylphenoxy side group designed to increase efficiency and LEDs using this material (SiPhO PPV) in a double layer architecture with a PEDOT HTL were studied.

$^1\text{H}$ -NMR spectra were obtained using a Bruker AM-300 spectrometer, and chemical shifts were recorded in ppm units against the residual proton solvent resonance (chloroform: 7.26 ppm). UV-Vis spectra were carried out with a Shimadzu UV-3100 spectrophotometer with baseline correction and normalization obtained using Microsoft Excel software. FTIR spectra were measured using KBr pellets and a Nicolet DX-5B spectrometer. The molecular weight and polydispersity of the polymer in THF solution were determined by gel permeation chromatography (GPC) analysis relative to polystyrene calibration. Emission spectra were made with dilute solutions ( $\sim 10^{-6}\text{M}$ ) on a Perkin-Elmer LS-50 fluorometer utilizing a lock-in amplifier system with a chopping frequency of 150 Hz. Solid-state emission measurements were performed using films supported on glass substrate and mounted with front-face excitation at an angle of  $< 45^\circ$ . For the measurement of EL, a light emitting diode was fabricated as reported earlier. For the double layer devices using PEDOT [poly(3,4-ethylenedioxythiophene)] as a hole injection/transport layer, a modified water dispersion of this polymer doped

with poly(styrene sulfonate) (PSS) (Bayer AG, Germany) was used. All processes and measurements mentioned above were carried out in air at room temperature.

Devices using PPV as a hole injection layer were also constructed using methods previously described. In these devices electron (PBD) and hole transport (PVK) materials were added to a mixed chromophore layer in which alternating block copolymers containing phenylene vinylene blocks were added to the SiPhOPPV to enhance efficiency.

The structural analysis of the polymers was confirmed by  $^1\text{H-NMR}$  and IR spectroscopy. The UV-visible, photoluminescence and electroluminescence spectra of the polymer are shown in Figure 1. The absorption spectrum of the thin film has a relatively sharp maximum at 450 nm with a band edge of 545 nm. The emission spectrum was obtained by excitation at the maximum absorption wavelength of the polymer. The maximum emission of the polymer was at 540 nm (yellow-green) with a shoulder at 575 nm. The EL spectrum of a SiPhOPPV device (ITO/PEDOT/SiPhOPPV/Li: Al) is almost identical to that of the PL spectrum and result indicates that EL of the device occurs at the same emission center as does PL in the SiPhOPPV film.

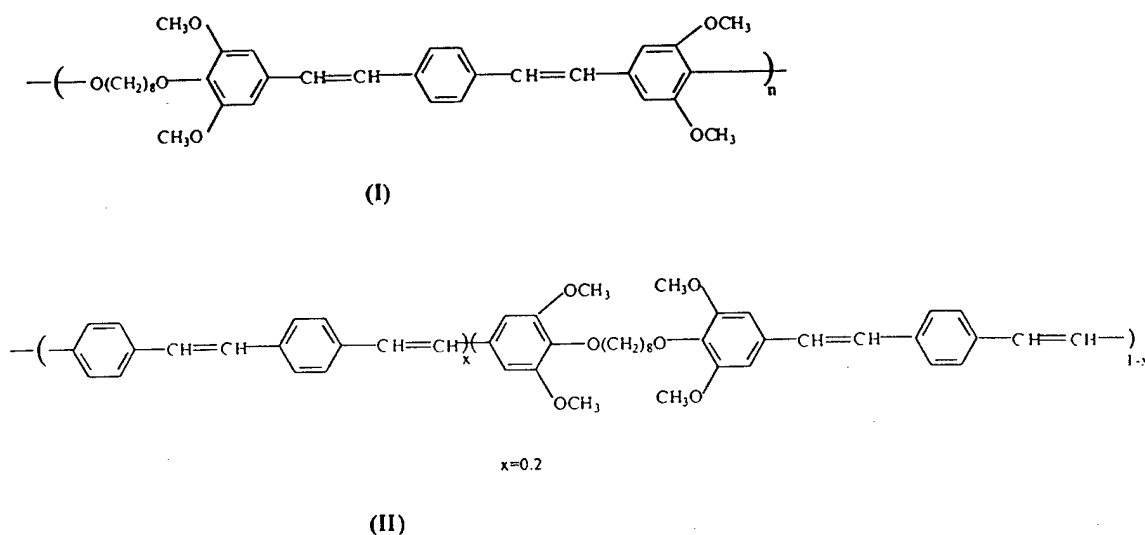


The work function and the surface roughness of the ITO substrate have important effects on the device performances such as turn-on voltage and luminance efficiency. Most  $\pi$ -conjugated semiconducting polymers have a HOMO level more than 5 eV relative to vacuum and there is therefore a significant energy barrier at the HOMO/ITO interface responsible for an increase in the turn-on voltage of the device. To facilitate hole injection, and to improve the luminescence efficiency, polyaniline (PANI) doped with camphor sulphonic acid (CSA) or polythiophene derivatives (PEDOT) doped with poly(styrene sulfonate) have been used as a hole-transporting layer and which also has the effect of smoothing the interface. In the present device PEDOT was used on the surface treated substrate. The turn-on voltages of devices with and without PEDOT are 6 V and 10 V, respectively. The introduction of a PEDOT buffer layer thus significantly decreases the turn-on voltage. The maximum efficiency of the SiPHOPPV single layer device (80nm on ITO glass) is 0.313 lm/Watt at 13.8 V with brightness of 44.3 cd/m<sup>2</sup>. The maximum brightness is 787 cd/m<sup>2</sup> at around 20V for this device. The brightness of the device increased to 2600 cd/m<sup>2</sup> at 23V when SiPhOPPV was used in a double layer configuration with PEDOT (25nm). The maximum efficiency of the double layer device was 0.24 lm/W at 12 V.

Multicomponent single and double layer devices were also prepared using the SiPhOPPV chromophore. Blends containing hole and electron transport materials and blends of blue and green chromophores were used in double layer device configurations in which PPV was interspersed between ITO and the

chromophore blend.

In these systems, PVK(Poly(N-vinyl carbazole)) and Butyl-PBD(2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole) were used as the hole and electron transport materials, respectively. The structures of the blue light emitting (I) and green light-emitting (II) alternating block copolymers are shown in Figure 2.



As a reference SiPhOPPV was also used in a single layer configuration without charge transport layers. In the double layer configuration, a PPV layer was used as a HTL to improve the longevity of the devices. The PPV layer thicknesses were 15 nm and 60 nm for the blue and green emitting blends, respectively. In this process, a PPV precursor was dissolved in methanol and spin-cast on ITO glass, eliminated at 250° under argon atmosphere for 2.5 hours. In the double layer devices, multi-component blends of selected compositions were spun-cast from chloroform solutions as a second layer onto the insoluble PPV. The Table below

shows the different configurations.

**Double layer, multi-component polymer blend compositions ratios**

Blend	PPV layer (nm)	PVK	Butyl- PBD	I	II	SiPhOPPV
BLUE						
1a	15	12	4	4	---	0.4
1b	15	12	4	4	0.4	---
GREEN						
2a	60	12	2	4	---	2
2b	60	12	2	4	2	---

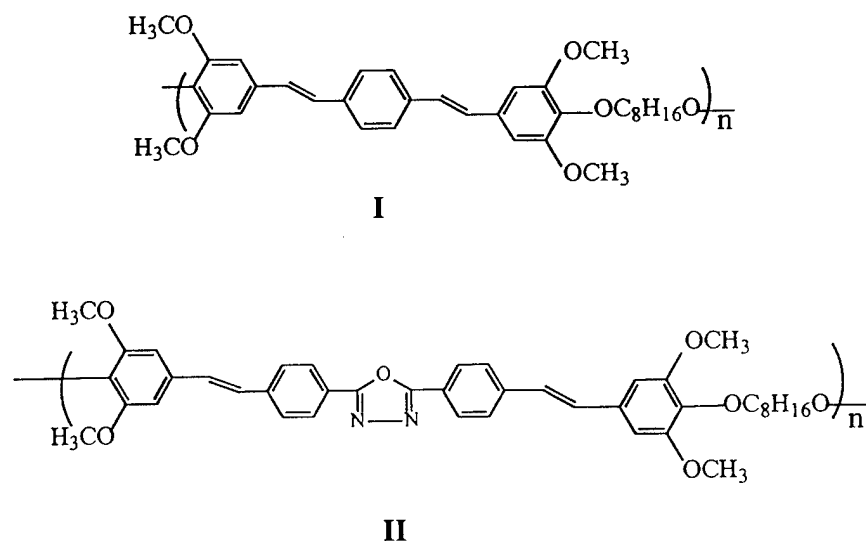
The SiPhOPPV is a strong green light emitting chromophore and it is of interest to further improve the EL efficiency of this chromophore by blending with hole and electron transporting materials as well as in multi-component chromophore architectures. For the blend used (2a) no blue shift or shoulder is observed in  $\lambda_{\text{MAX}}$  of the EL spectra because of higher concentration of the green emitter and EL intensity as well as device efficiency increases by a factor of 5, when SiPhOPPV is used in double layer blend configuration (blend 2a). The EL intensity and current density dependence on the applied dc voltage are more balanced (as compared to single layer devices of SiPhOPPV). The turn on voltage remains almost the same (5.5Volt) for both architectures. Thus alkylsilyl phenoxy derivative of PPV has been shown to be an efficient green light emitter in single and double layer LED configurations. In multi-component chromophore blends this derivative is more completely phase separated from other PPV derivatives whose properties had been previously shown to be enhanced in blends. This

more extensive phase separation and the resulting changed morphology facilitates efficient energy transfer and consequently in these combinations enhancement is present.

b) PPVs containing electron transport moieties in main chain

We have also designed and synthesized PPV derivatives containing rigid oxadiazole moieties in the main chain, II, Scheme 1. This polymer emits blue-green light, and can act not only as an emissive layer but also as useful electron transport layer in multilayer LEDs. The electron transport capability of the

**Scheme 1.** The structure of reference polymers.



copolymers was improved by this insertion; however the fluorescence quantum yield in chloroform showed a decrease compared to the reference polymer I due to



Single-layer LEDs based on polymers **III** and **IV** emit blue light at 476 and 478 nm respectively. The EL spectra are similar to the PL spectra, suggesting that both EL and PL originate from the same radiative decay process of the singlet exciton. The ITO/**IV**/Ca/Al LED gives a maximum brightness of 500 cd/m<sup>2</sup> at voltage of 22V. The maximum external quantum efficiency for the ITO/**III**/Ca/Al and ITO/**IV**/Ca/Al dLEDs that we observed are 0.035% and 0.11% respectively. For comparison, single layer devices based on **I**, **II** and two blends of **I** and **II** (4:1 and 1:1 wt/wt) corresponding to the compositions of **III** and **IV** were also fabricated under the same conditions. The peak wavelength of the electroluminescence spectra and the maximum external quantum efficiencies for these were measured and are shown in the table. Compared with the ITO/**I**/Ca/Al LED, the efficiency of the LEDs containing **III** and **IV**, i.e., ITO/**III**/Ca/Al and ITO/**IV**/Ca/Al, increased by a factor of 3 and 9, respectively, suggesting that the oxadiazole unit in the main chain enhances electron injection from the cathode and blocks the transport of holes injected from the anode through the emitting layer. This increases the probability of recombination with electrons at the emitting layer. The device based on the **I/II** blend (1:1 wt/wt) also gave a higher efficiency compared to devices containing **I** and **III**, indicating that the oxadiazole content plays an important role in the device performance. The devices based on **III** and **IV** showed higher efficiencies than the corresponding LEDs using blends of **I/II** (4:1 and 1:1 wt/wt respectively), indicating that the covalent incorporation of an electron transporting moiety is an effective way to improve the LED performance. The higher the



oxadiazole content, the lower the LUMO level of the polymer, therefore the better the electron injection.

Polymer	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (nm)	$\eta_{\max}^{\text{EL}}$ (%) <sup>a</sup>
	absorption	PL emission	EL emission	ITO/Polymer/Ca/Al
I	370	456	477	0.013
III	372	463	476	0.035
IV	370	465	478	0.11
II	368	473	494	0.004
I + II (1:1, Wt)	—	—	481	0.054
I + II (4:1, Wt)	—	—	477	0.015

<sup>a</sup>  $\eta_{\max}^{\text{EL}}$  was reached when the ratio of brightness to current density was maximized.

### c) Cyano-containing PPVs

Fully conjugated polymers based on cyano-modified PPV structures feature both good electron transport properties and efficient emissions at longer wavelengths in the visible spectra. The cyano group is responsible for the high electron affinity associated with these structures which is a desirable property because more stable metal electrodes, such as aluminum, can be used for electron injection.

To improve solubility and facilitate the processing of thin films on to electrode surfaces of PPV related polymers, bulky side groups are generally attached to the poly(1,4-phenylene vinylene) main chain, such as extended alkoxy

or alkyl groups in the 2,5-positions on the aromatic ring. Therefore, the cyano and extended alkyl or alkoxy side groups may occupy different relative positions in the PPV chain. The presence and relative position of these groups exert a large influence on the photoluminescent (PL) and electroluminescent (EL) properties.

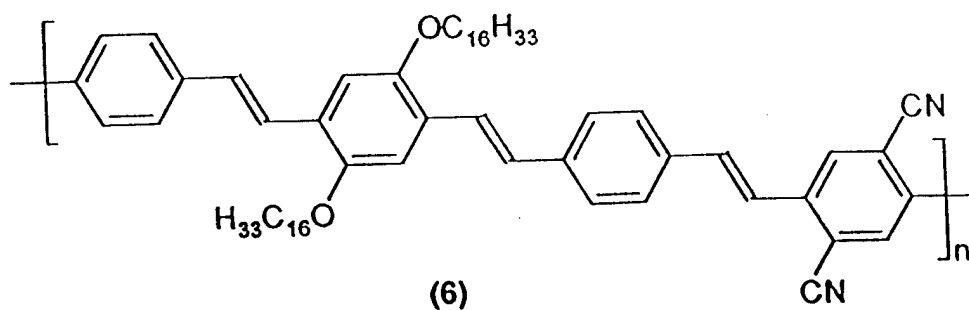
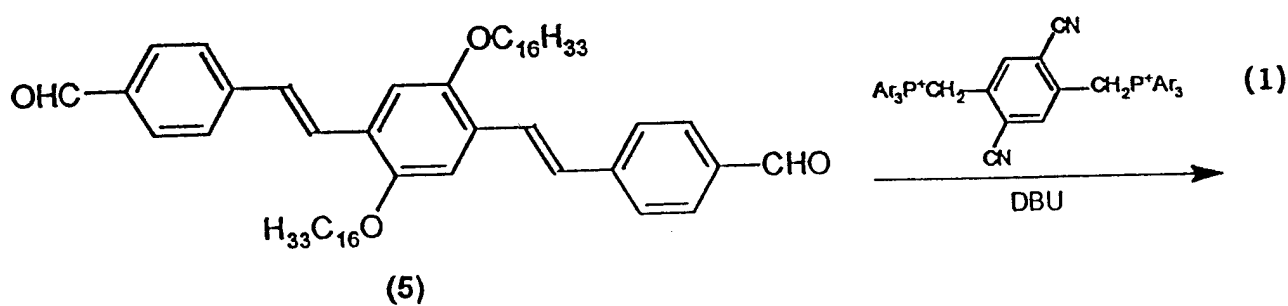
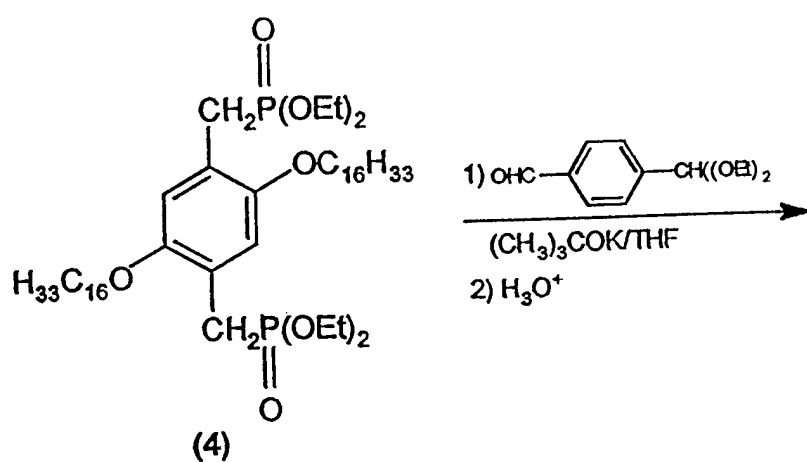
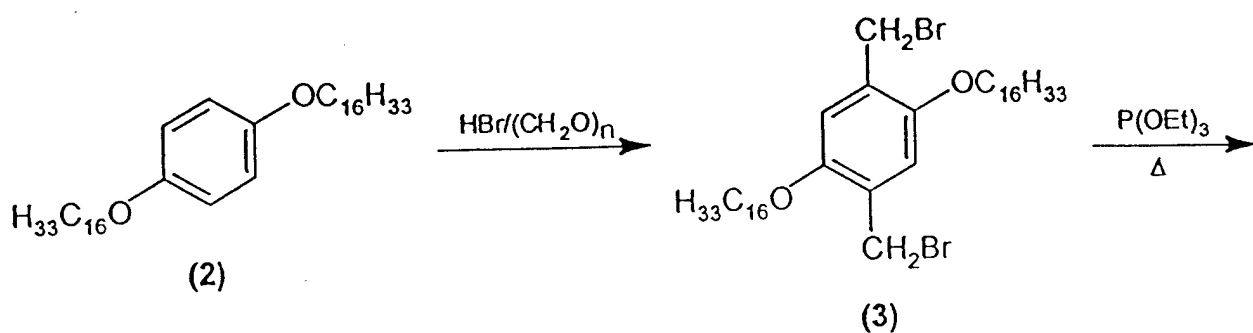
The substitution effects can be discussed in terms of steric and electronic contributions. The presence of long and bulky alkoxy or alkyl groups in the 2,5 aromatic positions in PPV brings about a weak steric interaction between neighboring units, which in some instances is responsible for a small blue-shift effect. The steric hindrance associated with these side groups in adjacent units prevents their coplanarity, decreasing somewhat the conjugation length and increasing the band gap of the emitting centers.

Most of the cyano-based PPV structures reported to date have had the cyano function linked to the vinylene group, and this also causes both steric and electronic effects. PPV-like structures bearing only the cyano group as a ring substituent have not been widely synthesized and characterized so far. Steric hindrance between cyano groups at the  $\alpha$ -vinyl position relative to the alkoxy or alkyl groups present in the 2,5 aromatic positions causes a blue-shift. When the steric hindrance is minimal, cyano-based structures bearing alkoxy groups exhibit a strong red-shift effect when compared to structures bearing only alkyl groups. Therefore, dipolar interaction between electron donor/acceptor groups is one of the structural requirements for production of strongly red-shifted emissions. Cyano modified PPV structures in which the cyano group is linked to the vinylene group

have been synthesized mostly via Knoevenagel reaction between aromatic dialdehydes and dicyanomethyl compounds in basic media. This method has some drawbacks because side reactions may take place, which precludes the production of defect-free structures. Conjugated polymers bearing cyano groups attached directly to the aromatic ring, which minimizes steric hindrance, have been synthesized via the Wessling soluble precursor scheme and thermal polymerization of 2,5-diiodo-3,4-dicyanothiophene.

A new structure with the cyano group linked to the central aromatic ring of the chromophore was synthesized by a Wittig reaction. For comparison, another structure with the cyano group linked to the vinylene function was synthesized by appropriate adaptation of a conventional Knoevenagel reaction. The Wittig-type polymerization produced a material with fewer structural defects together with a more strongly red-shifted emission. A monolayer LED device using the Wittig reaction product showed relatively higher emission intensity and stability than the Knoevenagel reaction product. This new technique for preparing cyano-based conjugated polymers via Wittig reaction was extended to produce a full conjugated cyano substituted polymer bearing long alkoxy groups which proved to be an efficient long wavelength emitter, Scheme 1.

An improvement of the emission properties was obtained from double layer devices of the type ITO/PPV/CP/Ca. Such devices turned on at 8V with conventional DC forward bias. A maximum luminance of ca. 3000cd/m<sup>2</sup> could be observed at 20V applied voltage. The EL spectrum obtained from this device



showed a slight blue-shift in relation to the single layer architecture, which indicates only a slight contribution of PPV emission. The high emission efficiency of this device can be attributed to several factors. The most important contribution comes from a better balance of opposite charge injection and their combination near the interface of PPV and the cyano polymer layers. This effect is inherent to multilayer devices composed of PPV and a good electron transporting material such as cyano-modified polymers. The enhanced stability of the device is another advantage of the double layer structure as the PPV layer provides improved mechanical and thermal stability.

As is well known, PPV is not only a good hole transport material, but also a good emitter, in principle having PPV as hole transport layer in a device can affect the color of the emission by involving PPV in the overall emission process. This depends on the thickness of the PPV layer, the relative location of energy bands of PPV and the emitter layer and the probability of electron transfer. The results indicate that in the present case the EL is mainly attributed to the cyano polymer and the PPV layer does not significantly contribute to the emission directly. As a result, a strong energy transfer process from PPV to the cyano polymer can be expected which is also supported by the large overlap between the emission of PPV and the absorption of the cyano polymer. In principle, EL processes involved in a double layer device (anode/PPV/emitter/cathode) may include the following:

- (1) Injected holes and electrons recombine to form excitons in both the PPV and the emitter layer near the interface. The excitonic energy in

the PPV layer will be transferred to the emitter layer, which gives rise to a single emission.

- (2) Injected carriers recombine to form excitons in both the PPV and emitter layers. These excitons decay independently in both layers, which produces a mixed emission spectrum.
- (3) Injected carriers recombine to form an interfacial complex at the interface between the PPV and the emitter layer. The interfacial excitons radiatively decay, which is responsible for an emitted color distinct from both PPV and the emitter layer.

The results of the very slightly blue shifted EL from ITO/PPV/CP/Ca compared to the single layer device ITO/Cp/Ca clearly favors the proposed process (1).

We also note that increasing the thickness of the PPV layer increases the probability of excitons formed in the bulk that cannot migrate to the cyano polymer layer. The radiative decay of a fraction of these excitons will produce light that will be emitted from the device from the PPV layer and the observed emission will therefore tend to blue shift with increasing thickness (from 15 to 90 nm). Changing the thickness of the PPV layer will also affect charge injection into the device. A thicker PPV layer requires a higher voltage for a given EL intensity, a thinner PPV layer facilitates hole injection from the anode because the energy bands of the PPV layer are tilted further due to the accumulated space

charge at the interface, which results in a EL intensity more sensitive to voltage change.

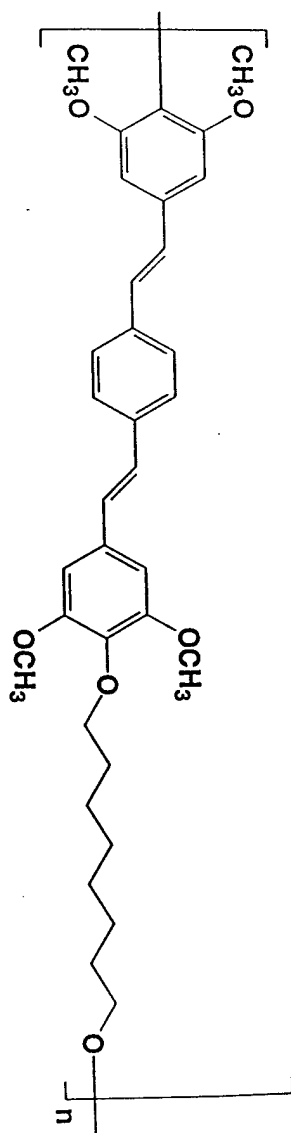
### Characterization

#### a) Phase separation

The copolymers used in the present studies contain short substituted phenylene vinylene sequences separated by methylene spacer groups in their structure. These copolymers were synthesized as described previously. The molecular structures of model compounds (copolymers **2<sub>8</sub>**, **3<sub>8</sub>** and bmppv) are shown below. The structures of **2<sub>8</sub>** and **3<sub>8</sub>** but not of bmppv could be regarded as homopolymers, however because of profound structural differences between the hard aromatic and the soft aliphatic sequences (blocks) in these chains, it was anticipated that full or partial phase segregation may occur.

A relevant comparison may be made to certain ionomers in which the dissimilarity of the underivatized segments and of the ion-containing segments is so large that clusters or domains of the latter are formed. The requirement for phase separation is not necessarily long block length but rather flexible chain containing two highly dissimilar segments. For some polyurethanes and for some ionomers thermal measurements provide a useful diagnostic tool for investigating microphase behaviour.

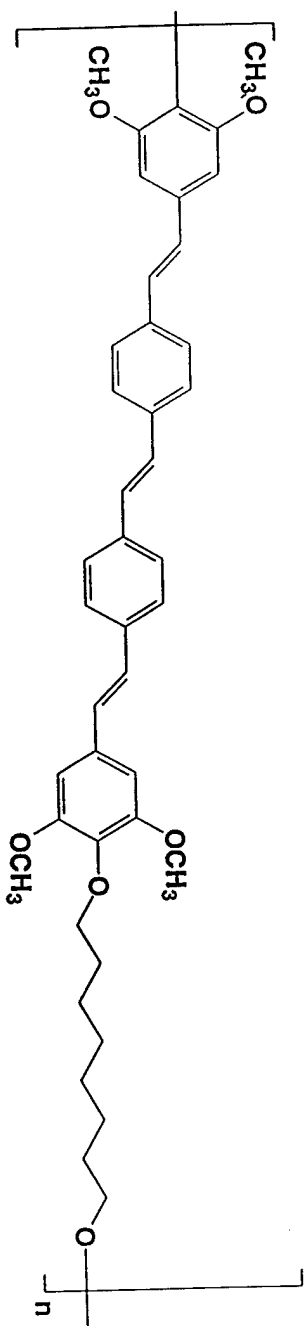
For the present systems it has already been shown that  $T_g$  drops systematically as the soft block length increases. We can ascribe the observed drop in  $T_g$  of the covalently anchored methylene sequences as their length increases, as being typical of the behavior of domains of essentially pure methylene sequences. There is also an alternative



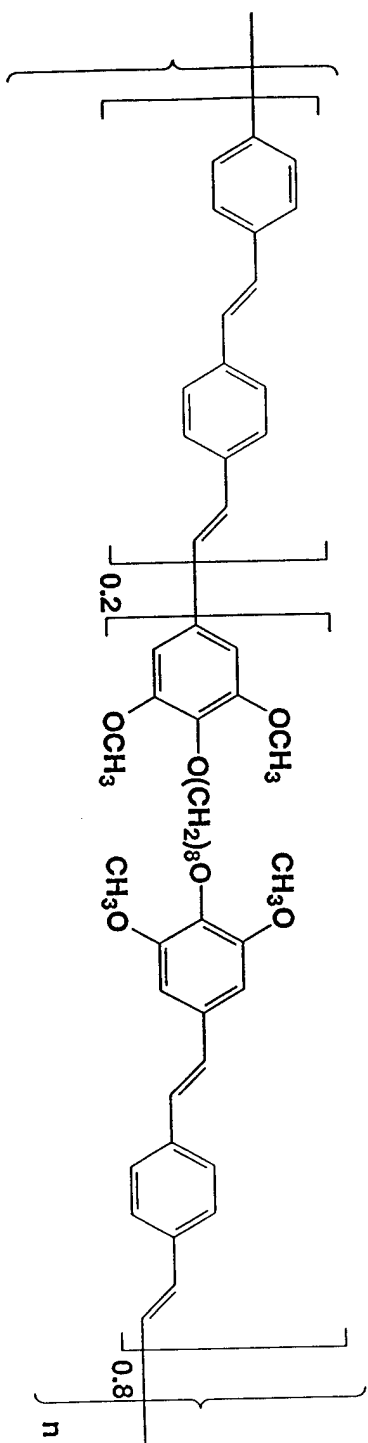
28

Hard Segment

Soft Segment



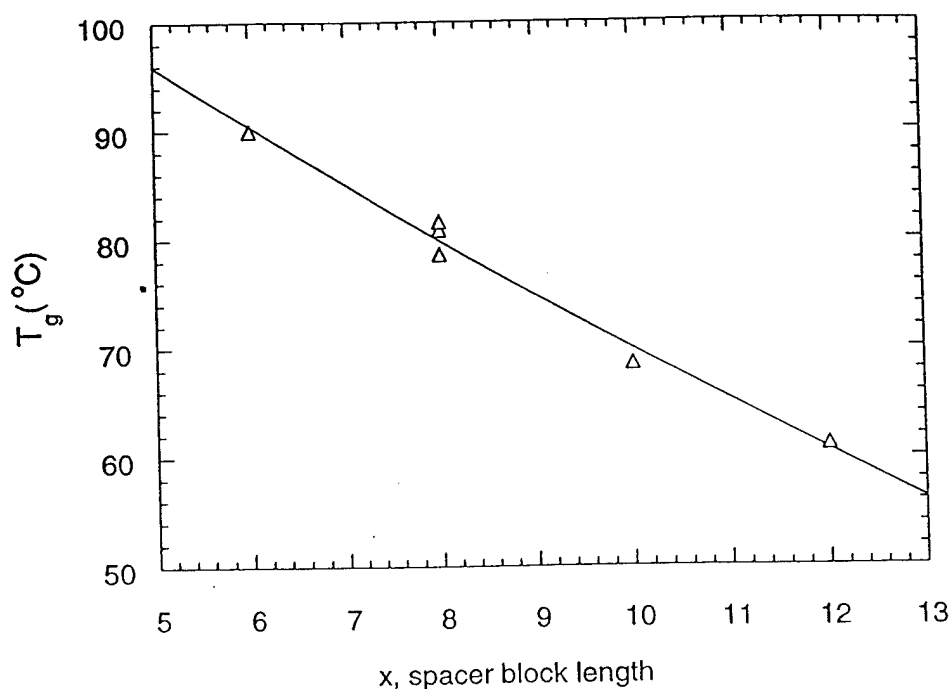
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bmppv



explanation, namely that there is phase homogeneity in these systems and the drop in  $T_g$  merely reflects the increase diluent content of the homogeneous hard/soft block mixture. The purpose of the study was to determine the extent of microphase separation occurring in the above copolymers. This was carried out a) by quantitative determination of the thermal transition parameters of the copolymers as a function of structure and b) by a study of selective plasticization of the soft block by a low molecular weight diluent, 1,12-dibromododecane (DBDD) chosen for its chemical similarity to the methylene sequences and its dissimilarity to the  $\pi$ -conjugated phenylene vinylene hard blocks. DBDD is a nonsolvent for the block copolymer itself; however, it was found to be an effective plasticizer in depressing the observed  $T_g$  of these systems.



The Figure shows glass transition temperatures ( $T_g$ ) as a function of the number of methylene units in the nonconjugated spacer blocks( $x$ ). The observed monotonic

decrease is consistent with previous work which attributed this glass transition to the segregated soft block in the copolymers.

The copolymers containing the same number of methylene units, (i.e. copolymers **2<sub>8</sub>**, **3<sub>8</sub>** and **bmppv**) exhibit identical glass transition, 79°C. The fact that the  $T_g$  is determined only by the soft block length and not by the nature of the hard block or the relative amount of soft block is consistent with the presence of a phase separated soft block. The absence of any observable thermal transition in these copolymers that can be associated with the hard block reflects the fact that such transitions would occur only above the decomposition temperature.

That phase segregation occurs in these systems is supported by the observation of selective plasticization behavior. The plasticizer used, DBDD is a non-solvent for the block copolymers but its chemical structure implies that a selective solvation of the soft block takes place. Such selectivity in solvation or plasticization is common in diblock systems but has been less frequently studied in multiblock structures. We observed a systematic decrease in the copolymer  $T_g$ 's with increase content of DBDD; again the changes are independent of the hard block. That is, the data show a uniform monotonic decrease on the addition of plasticizer of an eight methylene unit soft block, regardless of the nature of the hard block. Further quantitative assessment was provided by analysis of  $C_p$  changes at the glass transition of the pure copolymers and of the blends. The magnitude of the step change in the specific heat,  $\Delta C_p$ , accompanying the soft segment glass transition increases with increasing weight percentage of total amorphous phase that includes soft methylene blocks of the copolymers and the dibromododecane

plasticizer. We have calculated the  $\Delta C_p^s$  at  $T_g$  of the soft block for the  $2_x$  copolymer series from the data again assuming complete phase separation occur. Within experimental error, the results are constant,  $1.14 \pm 0.09$  J/g °C. A similar calculation for the  $2_8$  blends with DBDD yields  $1.28 \pm 0.15$  J/g °C. The change in heat capacity at  $T_g$  for DBDD is not known but it is higher than that of the soft block and therefore accounts for the difference in these two values. The constant values in both cases based on an excluded amorphous phase assumption, together with  $T_g$  results, lends validity to the concept of soft block segregation and selective plasticization. The domains are quite small and for the systems studied here were not detectable by either scanning or atomic force microscopy.

The present work distinguishes between a phase segregated and non-segregated model for a conjugated and non-conjugated multi-block alternating copolymer. Although the sequences are relatively short, the results of measurements of  $T_g$  and of  $\Delta C_p$  of the copolymers blended with plasticizer miscible only with the non-conjugated block favor a segregated model.

#### b) EL of mixtures

Two conjugated polymers, one emitting violet-blue light, the other emitting green light, were blended at different weight ratios. Only green emission with the characteristics of the second polymer was obtained in solid state PL of the blends, suggesting a Förster energy transfer between these polymers which was independent of the excitation wavelength. The large domains in the blend with higher concentration of the violet-emitting polymer were responsible for the incompleteness of energy transfer in such blends. In single-layer LEDs, the existence of an exciplex was also noted. The polymers,

PPV and PEDOT/PSS, used in double-layer devices improve device efficiency and reduce the turn-on voltage significantly. Almost complete Förster energy transfer phenomenon was found in double-layer LEDs. This work is pertinent to LED designs based on conjugated polymer blends aiming at tuning the emission color.

#### B. Polymer Blends (6,10,11,12,14,17,19,22,28)

Dielectric relaxation analysis can contribute to the understanding of the cooperative motion in blends because it is concerned with the movement of dipoles. In addition, because of the wide range of frequencies that can be covered, the relaxation spectrum can be obtained directly, rather than indirectly using time-temperature superposition. Such a spectrum reflects the state of the molecular dynamics of the segments, or group of segments, in the environment of other dipoles, or of nonpolar segments, in the heterogeneous or homogeneous domain.

This study is an extension of our earlier work on the PoCS copolymers and their blends with PS. In the present work a wider frequency range from  $10^{-3}$  Hz to  $10^6$  Hz, and a wider temperature range of 370K to 450K were employed. Utilizing these ranges of temperature and frequency it was possible to elucidate the nature of the molecular motions near to but above  $T_g$ .

The cooperative nature of segmental relaxations characterizes the  $\alpha$  relaxation. This is an intermolecular process, as opposed to the intramolecular cooperative relaxation typical of the  $\beta$  relaxation. When polymer molecules are in a "crowded" environment, the motion of a segment is interfered with due to the presence of its neighbor. Dissipation of energetic input, typically through a rotation of the segmental bond from one stable state to

another, is then possible only through the cooperation of the neighbors. Such cooperation comes in the form of a simultaneous relaxation. For two segments to move cooperatively, the probability of relaxation is squared, since each relaxation is an independent event. Thus, the cooperative relaxation time is  $\tau^2$ , with  $\tau$  as the relaxation time for a single segment in the absence of interference by neighbors.

At progressively lower temperatures, the volume decrease causes greater interference among neighbors. At high temperatures the cooperative relaxation involves two segments, called conformers. At lower temperatures the number involved increases to three, and then four, etc. The number of cooperating segments is defined as the size of the cooperative domain,  $z$ . This quantity occurs in the exponent of the Boltzmann probability for the relaxation rate process of Arrhenius form, so the apparent activation energy  $\Delta\mu$  for the single bond rotation is multiplied by  $z$ . As  $z$  increases with decreasing temperature, the apparent activation energy increases, transforming the Arrhenius form to the Vogel-Fulcher form. The temperature at which the latter diverges is  $T_0$  which is typically some 50 K below the empirical  $T_g$  obtained by DSC. At  $T_0$ ,  $z$  is supposed to approach infinity, but before this happens, the system will deviate from equilibrium, i.e., volume, entropy and enthalpy fail to keep up with the rate of cooling, and vitrification takes place.

We have analyzed the concentration fluctuations in terms of the distribution of  $T_0$  at a given temperature. Such a distribution is a measure of the domain size distribution, again, at that temperature. From this, we describe the concentration fluctuations in segmental terms, i.e., the local of nanoscale heterogeneity.

The broadband dielectric measurements were made on samples of PS, PoCS, a 50mol% PoCS/PS blend, and a 50mol%P(oCS/S) random copolymer, at temperatures between 370K and 450K. A single relaxation process was observed in each case. Both blend and copolymer show increases in the maximum values of  $\epsilon''$  with increasing temperature.

The data was fitted to a Vogel-Fulcher equation

$$\log f_{\max} = \log f^* - \frac{\Delta\mu^*}{R / \log e} \left[ \frac{1}{T - T_0} - \frac{1}{T^* - T_0} \right]$$

where  $f$  is the frequency of the loss maximum at a reference temperature  $T$ . At the divergence temperature  $T_0$  the cooperative entropy approaches zero, though the conformational entropy is far from zero.  $\Delta\mu^*$  is the Vogel-Fulcher energy, which is interpreted as the activation energy barrier to the rotation of a single conformer. The characteristic relaxation time  $\tau$  is equal to  $1/2\pi f_{\max}$ . The Vogel-Fulcher parameters were evaluated from the data.

The relaxation process observed is the  $\alpha$ -process corresponding to the cooperative relaxation of the conformers related to the micro-Brownian motion of the main chain. The observed values of  $\tau$  in PS and PoCS homopolymers are in agreement with the reported values and the temperature dependence of  $f_{\max}$  follows the Vogel-Fulcher equation. By defining the  $T_g$  as the temperature at which the dielectric  $\tau$  is 1s, agreement is obtained with the DSC  $T_g$ . The values of  $T_0$  are about 50K lower than  $T_g$  as expected.

The Vogel-Fulcher activation energies,  $\Delta\mu$ , of the blend, the copolymer and the homopolymer of PS are in good agreement with the reported values of about 12~15kJ/mol.

The frequency dependence of the complex permittivity  $\epsilon^*$  is frequently described by the empirical Havriliak-Negami representation,

$$\epsilon^*(\omega) = \epsilon'(\omega) - j\epsilon''(\omega) = \frac{\Delta\epsilon}{\{1 + (j\omega\tau_{HN})^\beta\}^\alpha} + \frac{\sigma_{dc}}{j\omega\epsilon_0} + \epsilon_\infty$$

where  $\epsilon'(\omega)$  is the real part,  $\epsilon_\infty$  is the dielectric constant at  $\omega \rightarrow \infty$ ,  $\Delta\epsilon$  is the relaxation strength,  $\tau_{HN}$  is the characteristic relaxation time of the Havriliak-Negami equation,  $\epsilon_0$  is the dielectric constant of vacuum,  $j$  is the imaginary unit and  $\sigma_{dc}$  is the dc conductivity. The Havriliak-Negami parameters were determined by a fitting procedure. The variables  $\alpha$  and  $\beta$  of Eq. 12 are empirical parameters that are related to the distribution of relaxation times. If the dipoles are able to orient independently,  $\alpha$  and  $\beta$  should be unity, and the process is of the Debye, single relaxation, type. In a system where correlation between dipoles exists, there is a distribution of relaxation times and  $\alpha$  and  $\beta$  are less than unity. One illuminating aspect of the  $\alpha$  and  $\beta$  parameters is that  $\epsilon''$  on the high frequency side of the peak is proportional to  $\omega^{\alpha\beta}$ , which is related to the distribution of domain sizes smaller than  $z$ , the maximum size that is a function of the temperature.

To consider the concentration dependence of domain size in the blends, we have analyzed the shape of the relaxation peak with fits to the Kolrausch-Williams-Watts (KWW) function:

$$\varepsilon^*(\omega) - \varepsilon_\infty = \Delta\varepsilon \int_0^\infty \exp(j\omega t) \left[ \frac{-d\varphi(t)}{dt} \right] dt$$

and

$$\varphi(t) = \exp[-(t/\tau_{KWW})^{\beta_{KWW}}] \quad 0 < \beta_{KWW} < 1$$

where  $\tau_{KWW}$  is the characteristic relaxation time of the KWW function, and  $\beta_{KWW}$  is the KWW parameter to describe the peak shape.

We assumed that the broadened  $\alpha$  relaxation can be considered as a result of superposition of relaxation mechanisms, the loss factor  $\varepsilon''$  was obtained from the distribution function  $P(\tau)$  as follows

$$\varepsilon''(\omega)/\varepsilon''_{\max} = \int_0^\infty P(\tau) \frac{\omega\tau}{1 + \omega^2\tau^2} d \log \tau$$

If the distribution is mainly due to dipole concentration fluctuations, then the function  $P(\tau)$  should be the normal distribution around  $\tau_{\max}$ , i.e.,

$$P(\tau) = \frac{1}{\sqrt{2\pi}\sigma} \exp \left\{ -\frac{(\log \tau / \tau_{\max})^2}{2\sigma^2} \right\}$$

where  $\sigma$  is the standard deviation of the normal distribution above.



In practice, the integral can be replaced by a sum of terms,

$$\varepsilon''(\log \omega) = K \Delta \log \tau \sum_{n=-20}^{20} P(n \Delta \log \tau) \varepsilon_A''(\log \omega - n \Delta \log \tau)$$

where  $n$  is a whole number, and  $\Delta \log \tau$  is 0.2, the same as the interval of the experimental data. The lower and upper limits of  $n$  were chosen to yield a sufficient range of  $\omega \tau$  to cover the whole relaxation process in the blend. There are 41 integer values of  $n$  between -20 and 20. We considered 41 different concentrations of blends, each having a different  $f_{\text{MAX}}$ . Each  $\varepsilon''$  was shifted along the  $\log \tau$  axis by  $n \Delta \log \tau$  from the center,  $\log f_{\text{MAX}}$  for the whole blend. Each of the  $\varepsilon_A''(\log \omega - n \Delta \log \tau)$  terms was weighted according to the  $P(\log \tau)$  function to account for the concentration distribution in the blend. From the above analysis, the following statements were

- (1) The broader spectrum of relaxation times for the blend than for the copolymer is due to the concentration fluctuation of the homopolymers in the blend being greater than those of the copolymer i.e. mixing in the blend is not as uniform as in the copolymer.
- (2) While the spectrum of the pure copolymer becomes broader at lower temperatures, the concentration fluctuations in the blend also become greater, as shown by the temperature dependence of  $\sigma$ .
- (3) As a corollary to (2) above, the random copolymers of the same composition could exhibit different degrees of broadening, depending on the sequence propagation constant, i.e., the size of the heterogeneities.

The origin of the broadening has been assumed to arise from the effective

distribution of local concentration fluctuations by many authors. However, their procedures for the quantitative estimation of the scale of the concentration fluctuations differ.

We considered the nature of concentration fluctuations affecting the relaxation behavior of blends, adopting the model of intermolecular cooperativity. In the presence of mechanical or electrical stress, a polymer molecule changes its unperturbed conformation to a less random conformation. The overall conformational change is the sum of rotations of bond angles in the main chain. To pass from one stable state to another, the bond angle must pass through a transient high energy state. The probability for this high energy state is the rate determining factor, and the chemical potential  $\Delta\mu$  elevated from the initial state is the activation energy for the relaxation. The relaxation time  $\tau$  is inversely proportional to the probability of reaching that energy barrier. If the relaxation time at some reference temperature  $T^*$  is defined as  $\tau^*$ , then the relaxation time  $\tau$  at another temperature  $T$  is given by

$$\tau = \tau^* \exp\left(\frac{\Delta\mu}{RT} - \frac{\Delta\mu}{RT^*}\right)$$

where  $R$  is the universal gas constant. We call the rotation unit a conformer, the smallest unit necessary for a conformational change.

In the condensed state, there is another factor that affects the relaxation time, and that is the interference from the neighbors that becomes increasingly important as the temperature is decreased. In the densely packed state it is assumed the rotation of a

bond into a new angle is often prevented by collision with a neighbor. To succeed, the rotation of the neighboring conformers must occur simultaneously. The probability for  $z$  conformers to relax simultaneously is the  $z$ -th power of the individual probabilities. The cooperative relaxation time is  $\tau^z$ . Taking a high enough reference temperature  $T^*$  at which  $z$  is 1, the cooperative relaxation time  $\tau$  is given by the formula

$$\tau = \tau^* \exp\left(\frac{\Delta\mu}{RT} z - \frac{\Delta\mu}{RT^*}\right)$$

$T^*$  is the temperature at which the relaxation is as fast as the frequency of the stress cycle, i.e.  $T^* \sim \Delta\mu/R$ . As  $\Delta\mu$  is about 3 Kcal/mol,  $T^*$  should be about 750K. We found  $T^*$  of 773K (500°C) and  $\tau^*$  of  $3 \times 10^{-12}$ s to be good values for a large number of polymers.

The temperature dependence of  $z$  is calculated from the ratio of an extensive quantity such as the entropy or the free volume with and without cooperativity.

The free volume can be considered to be the van de Waals excess volume,  $V_f$ , that is the difference between the liquidus and the solid volume. The latter is the crystalline volume, if the substance can be crystallized. If not, it may be estimated. The "occupied" volume of the glassy "state" is substantially greater, as it will be shown to be related to the cooperative relaxation. The free volume fraction  $f = V_f/V$  is often given by the formula:

$$f = \Delta\alpha T$$

where  $\Delta\alpha$  is the difference in the thermal expansion coefficients of the liquidus and the crystalline states.

The domain of cooperativity,  $z$ , grows larger as the temperature is decreased until it becomes large enough and the relaxation time is so great that the structural change cannot keep up with the decreasing temperature. This point represents the glass transition, and the temperature at which a transition occurs to a glassy non-equilibrium state is called the fictive temperature. The fictive temperature is lower if the cooling is slower which also results in a denser structure for the annealed glassy state.  $T_g$ , as measured by DSC will be higher for a more highly aged glass, because of the overshoot due to the greater relaxation time of the aged glassy state. The fictive temperature is at the border of equilibrium and non-equilibrium states, whereas  $T_g$  measured by DSC is not a thermodynamic quantity.

With decreasing cooling rates, the fictive temperature decreases, until finally, at the zero rate of cooling,  $z$  approaches infinity. The phenomenological temperature  $T_0$  is defined as the fictive temperature for the infinitely slowly cooled glass. Concurrently, the fractional free volume has decreased, but not to zero at  $T_0$ . While there still remains a certain amount of free volume, the interference among the neighbors has spread to the entire system, and cooperative relaxation has become impossible. The fractional free volume at  $T_0$  is defined as  $f_0$ .

One can also consider the entropy instead of the free volume. In that case, the domain size is proportional to the ratio of the conformational entropy  $S$ , and the cooperativity entropy  $s_{\text{coop}}$ . This will result in the Adam-Gibbs formulation for the cooperative relaxation time, from which the Vogel-Fulcher form of Eq. 11 can be again obtained.

We have shown that  $T_0$  is determined by the extra amount of free volume and entropy required for cooperativity. This does not, however, explain why  $T_0$  and  $T_g$  vary, sometimes widely, from material to material.

Entropy also depends on molar volume. The entropy decreases with increasing density, even if the conformation is kept unchanged. The probability of the spatial arrangements is dependent on the free volume, similar to the way the entropy of the ideal gas depends on the volume. For the ideal gas, this entropy is equal to  $k \ln V$ . For the free volume, this would be  $k \ln V_f$ . The absolute molecular volume has now entered in the calculation of  $T_0$ . When the temperature is changed from  $T^*$  to  $T_0$ , this volume related entropy decreases in proportion to the logarithm of the molecular volume, which varies with the size of the conformer. To set  $T_0$  as the critical temperature at which this entropy reaches the same critical value for all polymers of different conformer size, the following proportionality can be established between polymer A and polymer B:

$$(T^* - T_{0,A}) \ln M_A = (T^* - T_{0,B}) \ln M_B = c_3$$

where  $M_A$  and  $M_B$  are the molecular weights of conformers A and B, and  $T_{0,A}$  and  $T_{0,B}$  are the corresponding  $T_0$ ,  $c_3$  should be a constant for all polymers. This equation states, quantitatively, that a large conformer has a higher  $T_g$ . This equation has been supported empirically for more than 50 polymers, with values  $c_3=1750$ , and  $T^*=773K$ .

The average conformer sizes are  $104/2=52$  and  $139/2=68$ , respectively and thus  $T^*-T_0$  of 443 K and 415 K are obtained. With  $T^*=773K$ ,  $T_0$  of 330K and 358K are obtained. If  $(T_g-T_0)$  is assumed to be 46 instead of 50K, the corresponding  $T_g$  of 376K and 404K are obtained, in agreement with the data obtained by thermal analysis.

For the blend of PoCs and PS homopolymers, those domains that are rich in PoCS are larger than those rich in PS, not only in the average size of conformers but also in the number per domain,  $z$ . The frequency dispersion in  $\epsilon''$  is due to this difference among those domains with different sizes. It increases at lower temperatures, because the  $z$  of the PoCS rich domains grows faster than the  $z$  of the PS domains. For example,  $z$  for PS and PoCS are 2.41 and 3.10 at 433K, 285 and 4.03 at 413K, and 3.57 and 6.03 at 393 K, respectively. The corresponding broadening toward the lower temperatures is seen for the probability function  $P(\log \tau)$ . The breadth of  $P(\log \tau)$  rapidly increases at lower temperatures.

In the copolymer of the same composition as the blend this broadening is not observed, at least in this temperature range. It means that the domain of cooperativity remains more uniform. It is an indication that the sequence propagation is short with respect to aggregates of concentration fluctuations. If the sequence length of each comonomer unit is made longer, eventually it will approach a block copolymer and  $\epsilon''(\omega)$  should exhibit a broadening tendency similar to that of the blend.

The intensity of the loss peak of the polymer blend is apparently smaller than that of the copolymer, although the concentration of ICS units in the blend is the same as that in copolymer. To consider this difference, we estimated the structural factor (g-factor) from the relaxation strength. The effective dipole moment  $\mu_e$  per repeat unit is calculated from the Onsager equation,

$$\mu_e^2 = \frac{9kT}{4\pi N} \frac{\Delta\epsilon(2\Delta\epsilon + 3\epsilon_\infty)}{(\Delta\epsilon + \epsilon_\infty)(\epsilon_\infty + 2)^2}$$

where  $N$  is the number of dipoles per unit volume, and  $k$  is the Boltzmann constant. The reported values of 1.25 and 1.05 g/cm<sup>3</sup> have been used for the densities of PoCS and PS.

The  $g$ -factor is given by  $1+m\langle\cos\chi\rangle$ , where  $m$  is the average number of nearest neighbor dipole moments, and  $\langle\cos\chi\rangle$  is the average of the cosine of the angle between neighboring dipoles. If the dipole is isolated,  $g=1$ . The  $g$ -factor of the 50mol% copolymer is closer to unity than those of the homopolymers of PS and PoCS. This is explained by the fact that the polar *o*-chlorostyrene units are diluted by the relatively nonpolar styrene units, since the *o*-chlorostyrene units are diluted by the relatively nonpolar styrene units, since the *o*-chlorostyrene unit is dispersed homogeneously. However, the  $g$ -factor of the polymer blends is nearly the same as those of PS and PoCS. This means that the local conformational states of the PoCS chain are not perturbed by blending with PS, and the mixing of PoCS with PS does not occur on a segmental scale.

Thus effects of concentration fluctuations on the cooperativity in segmental motions from dielectric relaxation measurements carried out on the polymer blend 50mol% PoCS/PS, the copolymer 50mol% P(*o*CS/S), and the homopolymers PS and PoCS were analyzed. The observed relaxation process was assigned to the  $\alpha$  process due to a segmental motion in each case, since the temperature dependence of the frequencies of the observed loss maxima was of the Vogel-Fulcher type. The shape of the relaxation dispersion of the polymer blend was broader than that of the copolymer due to mixing heterogeneity in the former at the segmental level. The relaxation dispersion for the blend was deconvoluted to extract various relaxations arising from different local

concentrations. The shape of the curve at each concentration was obtained from the copolymer spectrum at the same temperature, which was taken to represent the relaxation of a homogeneous system. The probability,  $P(\log \tau)$ , for the peak positions of the deconvoluted process, which can be regarded as the distribution of relaxation times, was represented by a Gaussian distribution. The distribution,  $P(T_0)$  of the Vogel-Fulcher temperatures,  $T_0$  was estimated from  $P(\log \tau)$  by the Vogel-Fulcher equation. In this treatment,  $P(T_0)$  can be regarded as a criterion for the existence of heterogeneity at the segmental level. For example, if  $P(T_0)$  transforms to the distribution  $P(z)$  of the cooperative domain size, adopting the model of intermolecular cooperativity, the heterogeneity of the cooperative motion can be observed at each temperature. The g-factors for the various samples were estimated from the relaxation strengths. The g-factor was considerably larger (closer to unity) in the blend than either in the copolymer or homopolymers. This result supports the conclusion reached on the basis of dynamics that the local environment of the blend is heterogeneous at the segmental level.

### C. Solution Properties of Polymers (4,8,27,37)

A fundamental phenomenon in polymer science is the coil-globule transition of a single solvated macromolecular chain which occurs when a polymer is quenched from a good solvent into a poor solvent. This transition has been the subject of many investigations during the past four decades. Most coil-globule transition experiments have been carried out using polystyrene solutions of extremely low concentration. Various experimental methods such as static and quasielastic light scattering, small angle neutron scattering, ultracentrifuge and viscometric measurements have been used for the



determination of linear polymer dimensions. Two sets of contradictory experimental results for the contraction of polystyrene in cyclohexane have been reported, one yielding a very sharp transition with the other indicating a gradual contraction. Recent work extended coil-globule studies to highly dilute solutions of macromolecules containing polar groups, such as the halogenated polystyrenes, poly(4-chlorostyrene) and poly(2-chlorostyrene), and show that chain contractions can exceed those reported in earlier studies of the polystyrene/cyclohexane system. However, they are still not consistent with single globule formation.

We have studied the kinetics of the coil-globule chain collapse of PMMA in isoamyl acetate and n-butyl chloride by dynamic light scattering. Since the coil-globule relaxation time for a flexible polymer (PMMA) is rather fast, the earlier reported appearance of two-stage kinetics for the contraction process are not related to single chain collapse but rather to the aggregation of the polystyrene or poly(methyl methacrylate) molecules.

The extensive theoretical studies on heteropolymers have been motivated by their perceived relation to the protein folding problem. Theoretical treatments of copolymer collapse are increasing and a first-order coil-globule transition, unlike that in the homopolymer, has been predicted. In recent work, we have also studied the coil-globule transitions of random (statistical) and alternating copolymers of styrene and methyl methacrylate in various solvents and compared these results with the contractions observed in homopolymers. It was noted that in copolymers the temperature interval from the  $\Theta$ -state to that in the collapsed state was rather short compared to homopolymers.

We have now studied the coil-globule transition of poly(styrene sulfonate) in a 4.17

M aqueous NaCl solutions ( $\Theta$ -solvent) The hydrodynamic radius,  $R_h$ , of the polyelectrolyte was measured by a dynamic laser spectrometer.

Sodium polystyrene sulfonate has an extended chain conformation in pure aqueous solution due to the electrostatic repulsion between negative charges on the polyelectrolyte chain. If a salt is added to a dilute solution of NaPSS, the counterion condensation causes the polyelectrolyte chain to collapse. Measurements of contraction in dilute water solution of NaPSS in terms of  $R_h$  by the addition of small amounts of NaCl (5 and 100 mM) has been reported.

However, a further contraction of these chains was observed and globular forms were obtained at 10°C. The segment volume fractions at the globular states are estimated at 0.58 and 0.98 for two NaPSS samples studied in this work. This indicates that the density in the polymer domain of the globules is not dilute.

# VIII. PUBLICATIONS

Forty-six scientific papers (33 published, 13 in press) were completed with full or partial AFOSR support during the grant period.

1. Macromolecules, 32, 6933-6937 (1999) (with S.T. Pasco and P.M. Lahti) "Synthesis of Substituted Poly (*p*-phenylenevinylene) Copolymers by the Heck Method for Luminescence Studies".
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7. Phys. Rev. Letters, 83, 2588-2591 (1999) (with G.M. Mao, D. Chen and M.J. Winokur) "Generalized Anisotropic Planar Rotor Model and Its Application to Polymer Intercalation Compounds".
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